

THE NATURE OF PYROLYTIC OIL DERIVED FROM MUNICIPAL SOLID WASTE.

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The Occidental Research Corporation is developing a flash pyrolysis process for the production of fuels and chemicals. The main features of the process are near ambient pressure, no requirement for added chemicals, low capital investment, flexibility of feedstock (municipal refuse, coal, rice hulls, grass, tree bark), variability of temperature, and minimum feed pretreatment. Municipal solid waste is shredded; metals and glass are recovered and sold. The organic fraction, largely cellulose, is pyrolyzed. The resultant pyrolytic oil has a low ash content relative to the feedstock, and the oil can be burned for fuel value. The properties of this oil will be discussed in terms of analyses, viscosity, solubility, thermal stability, corrosion, and char content.

## HYDROGEN PRODUCTION FROM BLACK LIQUOR WASTES

by

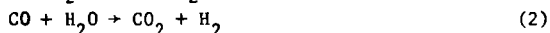
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INTRODUCTION

In a typical pulping process, approximately one-half of the raw material is converted to pulp and the other half is dissolved in the spent liquor. In the United States, nearly all of the spent liquor is concentrated and burned to provide part of the energy for the plant. One potential method of utilizing these liquors is to produce gaseous products for fuels, chemicals, and other applications. This suggestion is based on the following reasons: (1) the carbonaceous material of black liquor is well dispersed, (2) the black liquor contains considerable amount of alkali metals, which are known to have excellent catalytic effect on gasification, and (3) the concentrated black liquor contains about 40 to 60 percent of water, which can be converted to steam for the carbon-steam gasification reaction.

Because of the presence of carbonaceous material and water in the black liquor, it is suspected that the following water-carbon reactions would predominate:



Normally, the hydrogen concentration in the product gas should not exceed a certain limit imposed by thermodynamic equilibrium. For example, for a typical sodium-base spent liquor, the hydrogen concentration in the pyrolytic gasification products at 1000 K and ambient pressure will not exceed 60 percent in volume (1). However, in the presence of a  $CO_2$ -removal reagent, such as NaOH or CaO, etc., the equilibrium can be shifted

to drive reaction (2) toward completion. This would maximize the hydrogen yield, and, at the same time, reduce CO and CO<sub>2</sub> concentrations in the product gas.

The feasibility of utilizing the spent liquor via pyrolytic gasification at nearly atmospheric pressures has been demonstrated by Prahacs et al<sup>(1), (2)</sup>. They concluded that the Na-base liquor gave highest yields of hydrogen and carbon monoxide. However, the hydrogen in the product gas was generally in the range of 50-60 percent by volume. The objective of this paper is to demonstrate experimentally the technical feasibility of producing hydrogen-rich gas by pyrolytic gasification of black liquor. Sodium hydroxide was selected as a CO<sub>2</sub>-removal reagent for convenience of handling in a microreactor used in this study.

#### EXPERIMENTAL

The gasification experiments were conducted in a batch reactor system as shown in Figure 1. The reactor was made of a 12-inch-long 3/4-inch Inconel pipe (I.D. 0.742", O.D. 1.050"). Helium was used as an inert tracer to provide a material balance from which gasification yield was estimated.

In a typical experiment, the reactor was brought to the selected reaction temperature, evacuated, and then pressurized to 20 psig with helium. With valves V6 and V7 closed, a measured amount of water (0.5 cc, typically) was loaded into the sample reservoir through V5 by means of a hypodermic syringe and V5 was closed. The free space above the water sample in the reservoir was pressurized to 300 psig with argon (to serve as piston gas) and isolated by closing V4 before the water was forced into the heated reactor by opening valve V6 and immediately closing it. This provided a steam environment for gasification. With the same procedure, a measured amount of black liquor (2.0 cc) was then injected into the steam-filled reactor, except that 600 psig of helium pressure was

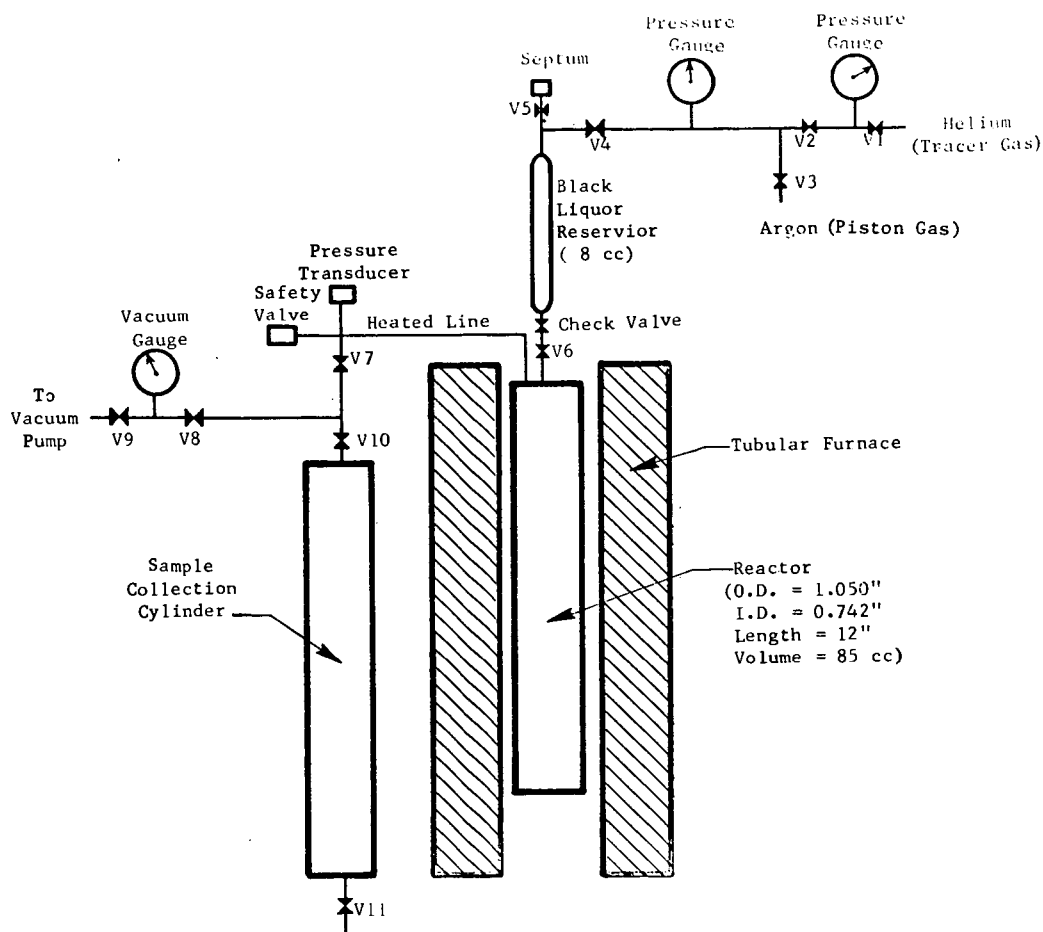


FIGURE 1. EXPERIMENTAL SETUP FOR BLACK LIQUOR GASIFICATION

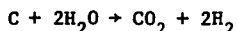
used as a piston gas. Vaporization of the solution took place almost instantaneously. After the predetermined reaction period, the products were collected by opening valves V7 and V10 to transfer the sample to the collection cylinder. The collected gaseous reaction products were analyzed by gas chromatography and mass spectroscopy.

All experimental tests to be discussed in this paper were conducted at 800 C. Two minutes were selected as the reaction time.

The sodium-base black liquor used in this study contained 15.6 percent by weight organic carbon. To investigate the addition of CO<sub>2</sub>-removal reagent, various amounts of sodium hydroxide were added to the liquor at Na/C mole ratios of 0.00, 0.38, 0.77, and 1.15, where Na is moles of added sodium and C is moles of organic carbon in the liquor.

### RESULTS

The results from the above-mentioned experiments are shown in Table 1 and Figures 2 and 3. The degree of gasification was estimated by assuming that hydrogen and carbon dioxide is produced according to the carbon steam reaction:



Therefore, for every two moles of hydrogen produced, one mole of organic carbon in the black liquor should be gasified. The carbon dioxide thus formed would react with NaOH to form sodium carbonate, up to the limit imposed by the quantity of NaOH added and/or already present in the black liquor. The following observations were made: the main reaction products were found to be hydrogen, methane, carbon dioxide, and carbon monoxide; very small amounts of C<sub>2</sub>-C<sub>6</sub> hydrocarbon (rarely exceeding 1.3 percent total) were observed; the concentration of hydrogen in the gaseous products was very high in all experiments, ranging from 62 to 88 volume percent.

TABLE 1. RESULTS OF PYROLYTIC GASIFICATION  
OF BLACK LIQUOR

Run No.	PG-01	PG-02	PG-03	PG-04
Temp (C)	800	800	800	800
Na/C Mole Ratio in Feed <sup>(1)</sup>	0.00	0.38	0.77	1.15
Product Yield (g-mole/1000 cc of as-received liquor)				
H <sub>2</sub>	6.85	11.96	16.77	18.35
CO	0.45	0.36	0.40	0.12
CH <sub>4</sub>	1.88	2.70	2.01	1.90
CO <sub>2</sub>	1.69	1.30	1.00	0.42
C <sub>2</sub> H <sub>4</sub>	0.008	0.012	0.007	NIL
C <sub>2</sub> H <sub>6</sub>	0.039	0.087	0.012	0.051
C <sub>3</sub> H <sub>6</sub>	0.002	0.007	0.003	0.006
C <sub>3</sub> H <sub>8</sub>	NIL	0.005	NIL	NIL
C <sub>6</sub> H <sub>6</sub>	0.005	0.12	0.077	0.08
Product Composition (%)				
H <sub>2</sub>	62.4	72.3	82.7	87.7
CO	4.1	2.2	2.0	0.57
CH <sub>4</sub>	17.1	16.3	9.9	9.1
CO <sub>2</sub>	15.4	7.9	5.0	2.0
C <sub>2</sub> H <sub>4</sub>	0.07	0.07	0.03	NIL
C <sub>2</sub> H <sub>6</sub>	0.35	0.53	0.08	0.24
C <sub>3</sub> H <sub>6</sub>	0.01	0.04	0.02	0.03
C <sub>3</sub> H <sub>8</sub>	NIL	0.03	NIL	NIL
C <sub>6</sub> H <sub>6</sub>	0.6	0.72	0.38	0.38
	100.33	100.09	100.11	100.02
Percent Gasification (based on carbon input)	40.0	64.0	72.5	75.6

(1) Na-content refers to the amount of NaOH added to the liquor.  
C-content is 15.6 wt %.

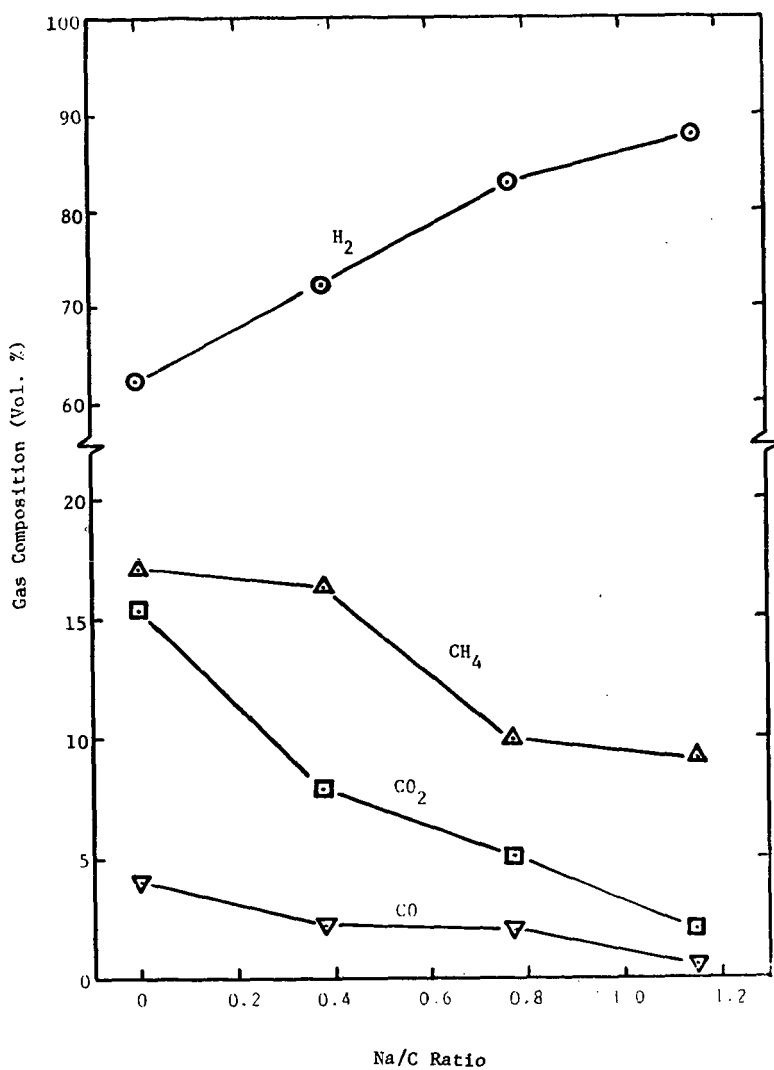


FIGURE 2. PRODUCT GAS COMPOSITION

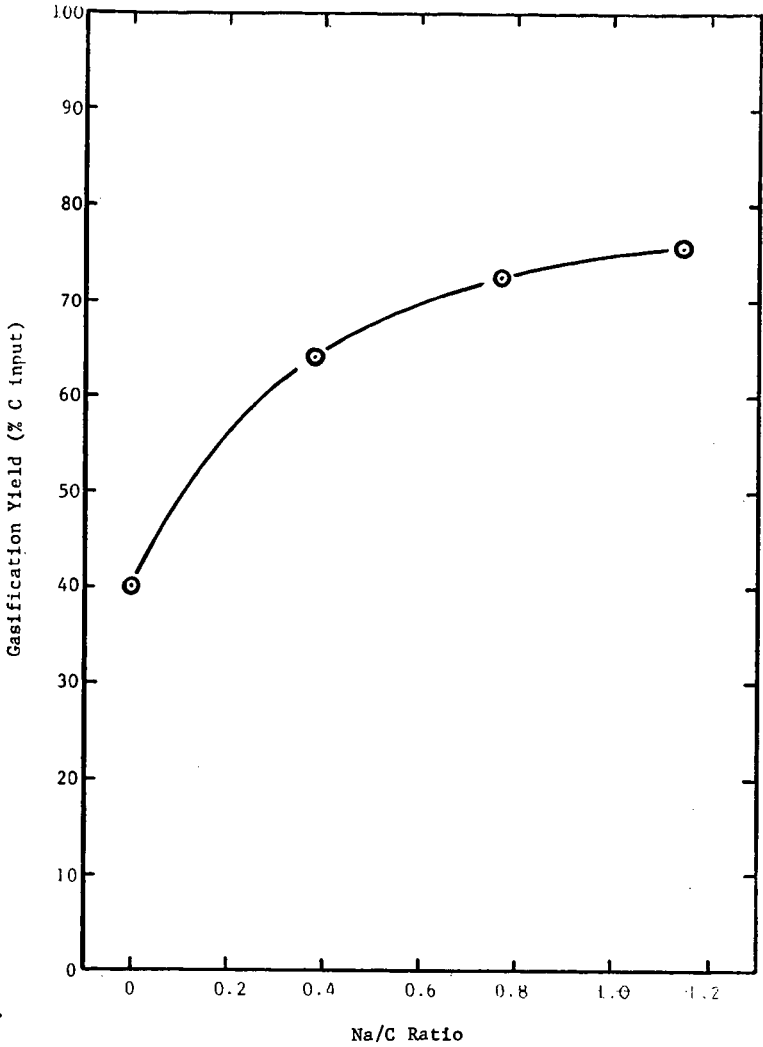


FIGURE 3. GASIFICATION YIELD



There are two striking effects of the added caustic soda on the gasification of black liquor. The first is the product-gas distribution, and the second is the total gasification yield. As shown in Figure 2, the hydrogen content of the gas increased with increasing Na/C ratio; about 88 percent of hydrogen was obtained with Na/C ratio of 1.15 as compared to 62 percent when no free NaOH (Na/C = 0.00) was added to the black liquor. Also, the CO and CH<sub>4</sub> concentrations, in general, decreased progressively with increasing Na/C ratio. The total gasification yield as a function of Na/C ratio is shown in Figure 3. Significant increases in total gasification yield with increasing Na/C ratio were observed. About 76 percent of conversion can be obtained at Na/C of 1.15, as compared to 40 percent, when no free NaOH was added to the black liquor. This suggests that the added alkali metal greatly enhances the gasification reaction.

#### CONCLUSIONS AND DISCUSSION

In conclusion, the production of hydrogen in concentrations greater than 85 percent in the gas from pyrolytic gasification of black liquor is technically feasible. The addition of caustic soda to the black liquor not only enhances the gasification reaction, but also increases the hydrogen concentration in the product gas. Other reagents, such as calcined limestone or dolomite, may be substituted for the caustic soda.

Thus, a waste material, which presents a disposal problem and a potential pollution hazard, can be converted to products for useful fuels, chemical feedstocks, and/or applications.

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## ECONOMIC CONSIDERATION AND ENERGY POTENTIAL OF AGRICULTURAL WASTES

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### Introduction

Bio-Gas of Colorado has been doing business as a company for two years dealing with treatment and reuse of agriculture waste organic materials.

We believe a commercially viable energy from the agricultural waste conversion industry potentially exists. This paper attempts to illustrate this statement.

Our research and studies have been conducted in Colorado, Arizona, Utah and New Mexico in conjunction with grants from the 4-Corners Regional Commission. Much of our design information has been accumulated from pilot plant operations and studies at the Monfort of Colorado Inc. beef feedlots. However, the information presented in this paper deals with Colorado exclusively.

### Background

Agriculture waste material such as steer manure has an energy value which ranges from 3000-8000 BTU per pound of solid material. This material currently is being used, almost exclusively, in its traditional manner as an addition to agricultural croplands. Various processes, well known and reported, are available to convert this manure into a form of energy product such as oil or gas.

The most often reported processes are:

- 1.) direct combustion
- 2.) pyrolytic conversion
- 3.) anaerobic digestion

Our studies have been exclusively concerned with the process of anaerobic digestion for reasons which will be discussed later.

### Definition

First, we'll discuss what we consider would be agricultural wastes of an energy producing nature. Specifically we have defined agriculture wastes as:

- 1.) Residue from animal husbandry operations
- 2.) Food processing wastes
- 3.) Crop residue left in the fields (or collected)

These materials are all generated in large quantities. Items one and two are in a reasonably centralized or collected form and are generated on a continuous basis. Item three is neither generated continuously or normally collected.

In Colorado, crop residues are not removed from the fields and most agriculture state agents strongly recommend leaving this material on the fields for erosion control in the windy climate.

### Amounts

Anderson(1) estimates 194.5 million tons of moisture and ash free organic material from animal husbandry operations are generated yearly in the U. S.

Burford (2) estimates that 1,065,500 tons per year of dry organic material (volatile solids) are collectable from 17 areas of concentrated livestock feeding in Colorado. The maximum distance considered for transporting manure was 15 miles. This information was generated during the summer of 1975 and represents approximately 52% utilization of the state feedlot capacity.

In Colorado, 8 areas or potential sites have been located in which the quantity of manure generated is large enough to justify a utility size methane facility.

### Available Energy

Before going into the amount of "deliverable" product such manure could generate, a discussion of the conversion process and the state of the "delivered" feedstock is in order.

Manure, as delivered, from an open dirt feedlot (found in Colorado or in the southwest in general) would be extremely variable in a) moisture content, b) dirt or grit ratio and c) extent of decomposition caused by exposure during the confinement period. Figure 1 shows decomposition and organic carbon loss in a typical manure sample versus exposure time. Figure 2 shows a typical steer manure as received per ton breakdown.

As mentioned earlier, our work has been exclusively devoted to the utilization of anaerobic digestion to process the manure. Manure as a "fuel" must be processed before direct combustion or pyrolytic decomposition could be practical. Anaerobic digestion however, would be less affected by moisture content, being a process whereby dilution with water is accomplished before utilization. Dilution allows the grit to be removed by simple sedimentation. The energy loss is less due to the water content than in other mentioned processes.

However, the main reason that digestion is viewed by the authors as the only viable process for utilizing the energy value of the manure is that the process allows the nutrient and humus values of the manure to be available to the farm community. Any process which destroyed nutrient and humus value of manure would be found in much disfavor by the agriculture community.

Anaerobic digestion is a process which utilizes bacteria to decompose (ferment) the organic fraction of the waste material.

The bacterial action is a complex process and a discussion of bacteria fermentation is neither the intent of this paper or practical in the time allowed, however, for those interested, a bibliography of excellent sources for this discussion is included in the reference section of this report. (3, 4, 5, 6)

Basically the following items are of importance in the efficient bacterial decomposition of organic material.

- 1.) Oxygen free environment - Those bacteria known as methanogenic bacteria are strict anaerobes and cease functioning in the presence of oxygen. This requires sealed tankage.
- 2.) Proper digestion time- The bacteria function at a rate proportional to temperature between 60-110°F (15.56-43.33°C) Mesophilic range, and 120-150°F (48.89-65.56°C) Thermophilic range.

At any given temperature enough time (minimum digester tank volume) must be provided to allow the methanogenic bacteria to properly process the organic material. A minimum time of 10 days is required at the Mesophilic temperature of 98°F, and 4.75 ft<sup>3</sup> of methane is generated for every pound of organic matter introduced into the system.

- 3.) Temperature uniformity - Although digestion will proceed at any of the temperatures mentioned, temperature changes greater than + 2°F in any 24 hour period are enough to cause "temperature shock", a phenomena whereby the bacteria become relatively dormant and gas production ceases. This requires a temperature control system and insulation of the digestion vessel.
- 4.) Nutritionally balanced feedstock - The bacteria require basically, organic carbon (lignin or non-organic forms of carbon will not digest), nitrogen, phosphorous and trace elements. Manure has enough of all the nutrients required. Increases in organic carbon alone could be tolerated with a resulting increase in gas production.
- 5.) Absence of toxic elements - Heavy metals and ionic material of high concentration can cause bacteria to cease functioning.

When the proper conditions are provided, the bacterial action can take place and the process of degradation or fermentation can take place.

The gas released from the process is known as bio-gas and roughly consists of 50%-70% CH<sub>4</sub>, 30% CO<sub>2</sub> and a trace of H<sub>2</sub>S by volume.

Our pilot plant consistently produced a gas of 55% CH<sub>4</sub> by volume (at Denver altitude) and verified that 4.75 ft<sup>3</sup> of CH<sub>4</sub> could

be generated for every pound of organic matter.\*

### Process Consideration

Figure 3 shows a basic flow schematic as proposed for the Monfort Gilcrest feedlot. This facility is sized to handle 100,000 cattle units of manure input. (A cattle unit is 1 animal of 1000 lbs weight). Again a complete description of the process (one of many proposed) is beyond the scope of this report but basically, the feed-manure is:

- 1.) mixed with water,
- 2.) sand and grit removed,
- 3.) the resulting slurry is heated and
- 4.) introduced into digestion vessels where digestion occurs.
- 5.) Bio-gas removed,  $H_2S$  and  $CO_2$  removed, compressed and sent into the interstate pipeline.
- 6.) Residue removed from digestion vessels, solids separated, remaining liquid is admitted to aeration basin.
- 7.) The liquid is aerated allowing aerobic bacteria to grow.
- 8.) Solids again separated and the remaining liquid remixed with manure.

### Plant Performance

A 100,000 cattle unit facility would input 1,200,000 lbs of dry solids per day to the plant. The plant will use 4 digester vessels of 1,000,000 ft<sup>3</sup> capacity each to provide the required detention time for bacterial action. Methane generated would be 3,406,000 ft<sup>3</sup>/day, at a cost of \$1.60 - \$2.00/1000 ft<sup>3</sup>. The bio-gas would be cleaned to the extent necessary and compressed to a pipeline pressure of 850 psig for sale.

### Digester Heating

Judicious use of insulation and heat exchange are required in the process to keep the net energy requirements as low as possible. A coal fired boiler will provide a majority of the net digester heating requirement. Augmenting heat sources will be waste heat of compression and solar energy. A form of flat plate collector using digester effluent as the heating medium has been patented and incorporated into the system design.

### Capital Costs

Bio-Gas of Colorado has been engineering on this facility for 2 years and our latest capital cost estimate shows a \$5,500,000 - \$6,500,000 cost for this facility. (\$1,610 - \$1,910 capital cost per generated MCF) Figures 4 and 5 show capital cost figures for digestion systems of various sizes as explained on each figure.

\* On a theoretical basis the breakdown of 1 lb of cellulose would yield 7 ft<sup>3</sup> of methane. 4.75 ft<sup>3</sup> is an actual yield.

We have built several of the smaller sizes as shown on figure 4, and these figures include 40% markup over cost for the builders.

Figure 5 is estimated and assumes costs as related to an owner-operator, however, IDC and contingency of 15% are allowed in figure 5. As can be seen from 10,000-100,000 cattle units is the least size sensitive area on the curve and 40,000-50,000 cattle units would be required to "make the deal" interesting to anyone contemplating a manure/gas facility.

Some explanation of construction techniques is in order to justify figure 5.

The process flow schematic is relatively simple. The facility consists basically of large tanks and lagoons for holding slurries and allowing anaerobic and aerobic bacteria to process the material feedstock. The physical size of the tanks required to allow the proper hydraulic detention time is the feature which causes the largest increment of capital cost in the envisioned facility. Traditional sewage plant design relies on concrete and/or steel tanks, each custom engineered and field erected.

A factor cost much reported for these municipal installations is \$2.00/ft<sup>3</sup> of digester volume.

In the envisioned facility, all tanks including the digester vessels themselves, the clarifiers and lagoons are all "Hypalon-lined" in-the-ground-trenches, a type of construction finding favor in more recent waste treatment projects. Use of this type of construction has allowed keeping the total capital costs under \$2.00/ft<sup>3</sup> for this type of facility. This includes the extra equipment such as slurry mixing, gas cleaning and compression, and liquid aeration that a municipal facility would not require.

### Conclusions

It is our contention that a potentially viable energy producing industry could be operated in Colorado and in other agriculturally oriented states for the following main reasons:

- 1.) Manure is available in "commercial" quantities in a collected form.
- 2.) Today manure is available at \$2.00/ton or less (\$.615 - \$.705 million BTU). As a fuel manure today is cheaper than coal.
- 3.) The technology is well known to convert the energy value of manure into a very desirable form.
- 4.) It appears the cost of capital for the conversion facility (under \$2,000 per generated MCF) is also desirable.

TABLE 1

## COLORADO MANURE INVENTORY AND GAS PREDICTION

Per Animal	Cattle	Dairy	Hogs	Sheep	Chickens	Turkeys
Solids Per Animal						
Total dry solids	12.0	13.2	1.12	.5	.073	.20
Percent volatile solids	80%	80%	85%	80%	76%	76%
Volatile solids/day	9.6	10.56	.95	.40	.055	.15
Expected volatile solids <sup>1</sup>						
scraped per animal/day	7.17	8.44	.76	.32	.055 <sup>2</sup>	.12
Methane (CH <sub>4</sub> ) Potential						
Animal Basis:						
Livestock in all 17 Site Areas	676,218	36,050	104,000	258,000	1,997,000	3,455,000
Livestock in "Big 8" Site Areas	565,364	22,100	80,000	254,000	1,946,000	3,415,000
Gas potential (MCF CH <sub>4</sub> /day) <sup>3</sup>						
in all Site Areas	23,030	1,445	375	391	522	1,969
Gas potential <sup>4</sup> in "Big 8" Site Areas	19,255	885	289	386	508	1,947
Total Gas Potential						
In all 17 Site Areas			27,733,000 ft. <sup>3</sup> per day			
In "Big 8" Site Areas			23,270,000 ft. <sup>3</sup> per day			
In "Big 8" with collectable factor applied			21,022,000 ft. <sup>3</sup> per day			

<sup>1</sup>This includes a 6% initial volatile solids loss in run-off and 15% loss due to decomposition during the six month cleaning period (average manure age of three months).

<sup>2</sup>Weekly cleaning as opposed to deep pit operation.

<sup>3</sup>Methane (CH<sub>4</sub>) production per pound of volatile solids equals 4.75 ft.<sup>3</sup> per pound.

<sup>4</sup>Sites 1, 5, 6, 7, 8, 9, 12, 14.

<sup>5</sup>Cattle, 100% manure from lots 1,000 head or greater, 60% from lots less than 1,000 head; 60% from Dairy waste; 50% from Hog, Sheep, Chicken, and Turkey operations is collectable.

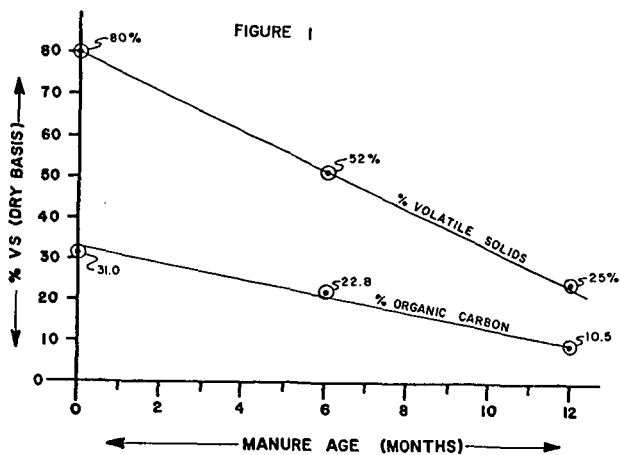


FIGURE 2  
PLANT INPUT & OUTPUT  
ON UNIT WET TON BASIS

• Expected manure scraped → 4.0 Ton per head per year

• Input - Output:

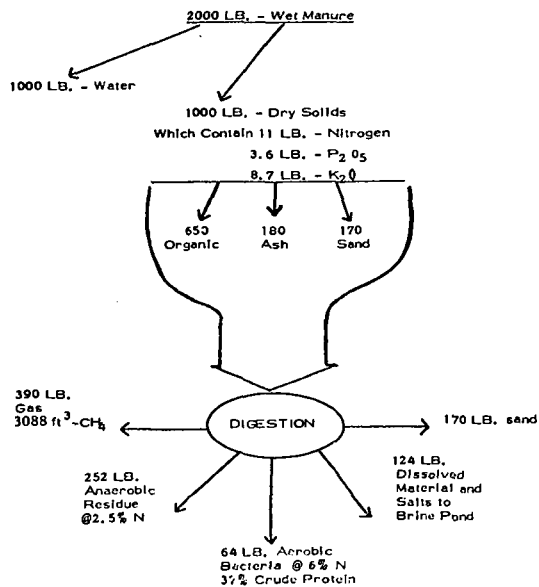
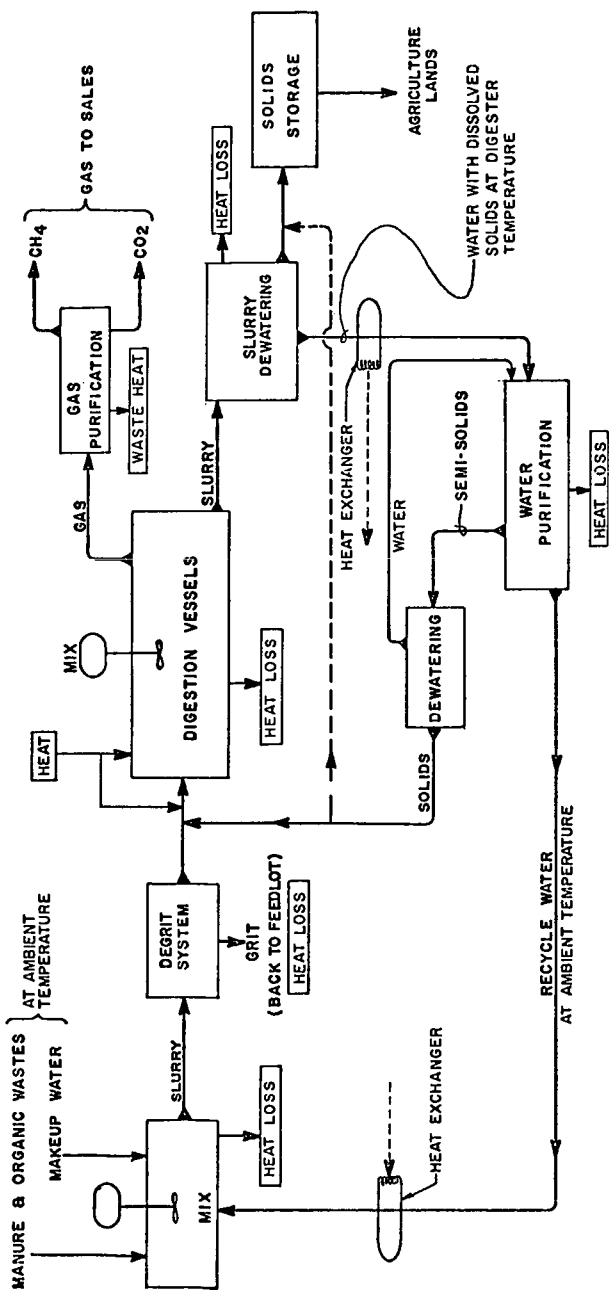


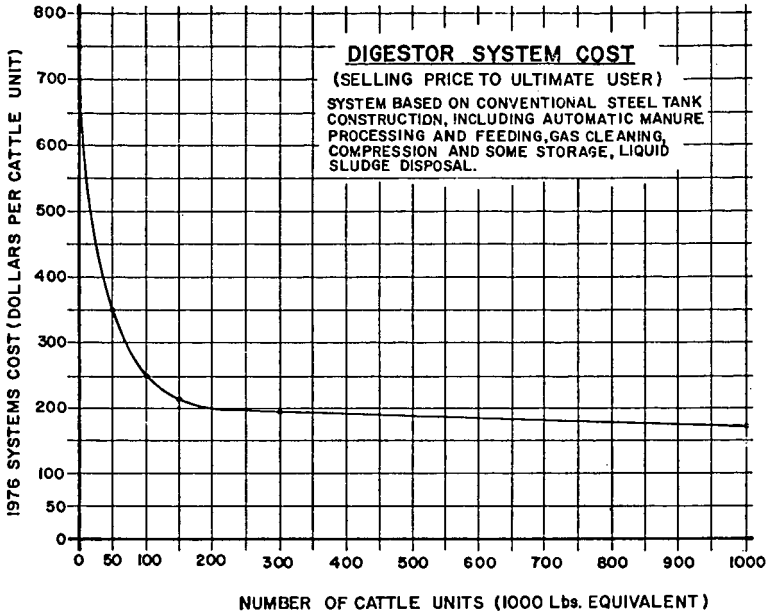


FIGURE 3



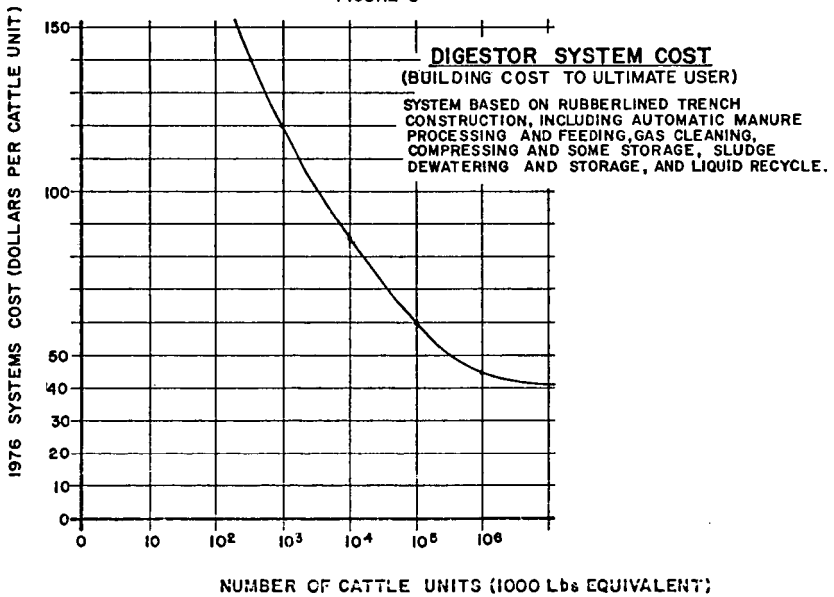
# MAJOR BLOCK DIAGRAM AGRICULTURE WASTE/GAS PRODUCTION

FIGURE 4



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FIGURE 5



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PIPELINE GAS FROM SOLID WASTES BY THE SYNGAS RECYCLING PROCESS. H. F. Feldmann,

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A two-stage process for converting solid wastes into a methane rich gas capable of being upgraded to pipeline quality is described. In the first zone, the raw solid wastes are contacted with a hydrogen containing gas and are converted to hydrocarbon gases consisting mostly of methane with smaller amounts of ethane, carbon oxides, carbonaceous char and less than one percent oil. The char is used in a second stage connected reactor to generate a synthesis gas for the first stage. Results of continuous operation of the first stage as both a moving-bed and free-fall reactor are presented and these data are combined with gasifier performance calculations to establish large-scale performance characteristics of the integrated system.

## THE GASIFICATION OF WASTES USING MOLTEN SALTS

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## INTRODUCTION

This paper describes some experimental results showing the technical feasibility of producing a low Btu gas (100-150 Btu/scf) from wastes using molten salt technology. The concept of molten salt gasification is described first and is followed by a description of the experimental apparatus. Then some results of bench scale gasification tests of selected wastes are given.

The disposal of waste x-ray film is discussed. While low Btu gas can be produced with film, a more important objective is to recover the silver from the film. Therefore, experiments to recover silver as well as experiments producing low Btu gas are described.

The discussion of film tests is followed by tests in which rubber tires and paper are gasified.

Then, some tests on the disposal of nitropropane are described. Organic  $\text{NO}_2$ -containing compounds can be present in other wastes and, since they are a source of nitrogen oxides emissions due to their high nitrogen content, tests were carried out to determine if such wastes could be disposed of with low  $\text{NO}_x$  emissions.

The experimental portion of the paper concludes with a description of some gasification tests with sugar. Sugar was tested because it is a well-characterized oxygen containing substance and has a composition typical of many solid wastes.

A discussion of the results, including a comparison of these results with those of coal and oil gasification using the same technology, concludes the paper.

#### CONCEPT OF GASIFICATION OF WASTES WITH MOLTEN SALT

Molten Salt Gasification of wastes is a process which provides for the removal of pollutants during an initial partial oxidation and gasification step followed by complete burning of the clean combustible gases in a secondary combustor. Thus, the Molten Salt Gasification Process for the disposal of wastes is a two-step process.

In the first step, shredded combustible waste and air are continuously introduced beneath the surface of a sodium carbonate-containing melt at about  $1,000^{\circ}\text{C}$ . The waste is added in such a manner that any gas formed during combustion is forced to pass through the melt. Any acidic gases, such as  $\text{HCl}$  (produced from chlorinated organic compounds) and  $\text{H}_2\text{S}$  (from organic sulfur compounds) are neutralized and absorbed by the alkaline  $\text{Na}_2\text{CO}_3$ . The ash introduced with the combustible waste is also retained in the melt. Any char from the fixed carbon is completely oxidized in the salt. The temperatures of gasification are too low to permit a significant amount of  $\text{NO}_x$  to be formed by fixation of the nitrogen in the air. Gasification of the waste is accomplished by using deficient air, i.e., less than the amount of air required to oxidize the waste completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, in the first step, the waste is partially oxidized and completely gasified in the molten salt furnace. The gas generated has an effective heating value which depends upon the original waste. Values of approximately 150 Btu/scf have been obtained.

In the second step, this gas flows to a conventional gas-fired boiler in which it is combusted with secondary air, producing steam.

As a possible option, a sidestream of sodium carbonate melt can be withdrawn continuously from the molten salt furnace, quenched and processed

in an aqueous regeneration system which removes the ash and inorganic combustion products retained in the melt and returns the regenerated sodium carbonate to the molten salt furnace. The ash must be removed to preserve the fluidity of the melt at an ash concentration of about 20 weight %. The inorganic combustion products must be removed at some point to prevent complete conversion of the melt to the salts, with an eventual loss of the acid pollutant-removal capability.

This concept is the basis of the Molten Salt Coal Gasification Process which is currently being developed by Atomics International.

In the molten salt concept for silver recovery, the film is gasified in a  $\text{Na}_2\text{CO}_3$  melt in the same manner as other combustible waste. The silver from the film forms a liquid metal pool which is drained from the bottom of the combustor to form metal ingots with a purity exceeding 99.9%.

## EXPERIMENTAL

### Materials

The waste x-ray film was analyzed and was found to contain in weight %: carbon, 53.2; hydrogen, 5.5; ash (which was essentially silver), 2.4; and the oxygen (by difference), 38.9. Direct analysis for silver showed that the film contained 2.3% silver. The wood was pine sawdust with a moisture content of 2.8%. No chemical analyses were carried out, but a typical composition for pine wood on a dry basis is: carbon, 51.8; hydrogen, 6.3; ash, 0.5; and oxygen, 41.3. The heating value is typically 9,130 Btu. The rubber was buffings from an automobile tire tread. No chemical analyses were carried out. The nitropropane was practical grade obtained from Eastman. The sugar consisted of pure sucrose. The  $\text{Na}_2\text{CO}_3$  for the salt bath was technical grade material obtained from Kerr McGee.

### Bench-Scale Molten Salt Gasifier

A cross-section view of the bench-scale molten salt gasifier is shown in Figure 1. Approximately 12 lb of molten salt are contained in a 6-in. ID

and 30-in. high alumina tube placed in a Type 321 stainless steel retainer vessel. This stainless steel vessel, in turn, is contained in an 8-in. ID, four-heating zone Marshall furnace. The four heating zones are each 8 in. in height, and the temperature of each zone is controlled by an SCR controller. Furnace and reactor temperatures are recorded by a 12-point Barber-Colman chart recorder.

Solids, pulverized when necessary in a No. 4 Wiley mill to  $<1$  mm in particle size, are metered into the 1/2-in. OD central tube of the injector by a screw feeder. Rotation of the screw feeder is provided by a 0 to 400 rpm Eberback Corporation Con-Torque stirrer motor. In the injector the solids are mixed with the air being used for gasification, and this solids-air mixture passes downward through the center tube of the injector and emerges into the 1-1/2-in. ID alumina feed tube. This alumina feed tube is adjusted so that its tip is  $\sim 1/2$  in. above the bottom of the 6-in. diameter alumina reactor tube. Thus, the solids-air mixture is forced to pass downward through the feed tube, outward at its bottom end, and then upward through  $\sim 6$  in. of salt in the annulus between the 1-1/2-in. and the 6-in. alumina tubes. In the case of liquids, a different feed system is used. The liquid is pumped with a laboratory pump and is sprayed into the alumina feed tube.

In order to prevent the melt temperature from rising when an excessive amount of heat is released to the melt, a cooling system (not shown in Figure 1) cooled by air, maintained a constant temperature. It consists of an eight-hole air distribution ring, mounted underneath the stainless steel ceramic tube retainer vessel. Air at rates up to 18 cfm can be passed upward between the outer surface of the retainer vessel and the furnace wall.

#### Off Gas Analyses

Samples of the exit gas, for analysis by gas chromatography, are taken with 1-ml gastight syringes downstream of the  $\text{CO}_2$  analyzer. Two gas samples



are taken at the same time. One sample is analyzed for carbon monoxide, oxygen, and nitrogen, using a molecular sieve 13X column at room temperature. The other sample is analyzed for carbon dioxide, methane, ethane, ethylene, sulfur dioxide, and hydrogen sulfide, using a Poropak Q column at 130°C (266°F). Often, continuous measurements of NO<sub>x</sub>, CO, and CO<sub>2</sub>, are taken of the off-gas. The NO<sub>x</sub> analyses are made with a Thermo Electron Corporation Chemiluminescent NO<sub>x</sub> Analyzer. The carbon monoxide and carbon dioxide determinations are made with Olson-Horiba, Inc. units. (Mexa-300 carbon monoxide and Mexa-200 carbon dioxide analyzers, respectively.) All gas analysis data are reported on a dry basis.

### Results

The gasification steady state results for film, wood, rubber, and nitropropane are shown in Table 1. The results for sucrose are shown in Table 2.

#### Film

Two series of tests were carried out with waste x-ray film. The purpose of the first test (No. 1) was to show that pure elemental silver could indeed be recovered under gasification conditions attainable in the Atomics International pilot plant which is capable of gasifying about 200 lbs/hr of coal and waste. A combustible gas with a higher heating value (HHV) of 100 Btu/scf was obtained. In this bench scale test, 15 lbs of film were burned. After the test, the melt was cooled until the silver solidified (960°C). A bright pellet of lustrous silver metal having a weight of 0.34 lbs was recovered. This corresponds to 98.6% of the silver in the film feed. Because of the successful results of this bench scale tests, a test to recover film from 20,000 lbs of waste x-ray film is planned for the near future. (A silver recovery test in the Atomics International's pilot plant has been carried out in which 15,000 lbs of waste x-ray film were burned under excess air conditions at a rate of 100 lbs/hr. In that test, which was carried out for the Navy, a single silver metal ingot weighing 230 lbs with 99.9% purity was recovered.)

In test No. 2, the gasification was carried out under more reducing conditions (22% theoretical air). This time a gas with a much higher heat content was obtained (179 Btu/scf). Elemental silver was recovered from this test also but the yield was not determined.

#### Wood

Gasification of the pine wood was carried out with 30% theoretical air. Again, a gas with a high heat content (181 Btu/scf) was obtained. The  $H_2$  content was somewhat higher and the  $CH_4$  content somewhat lower than was obtained with the film at 22% theoretical air. However, it is not clear whether this difference is real.

#### Rubber

Two tests were carried out with rubber from a rubber tire. Since the tire contained organic sulfur which would form  $Na_2S$  in the melt, the  $Na_2CO_3$  melt originally contained 6 wt %  $Na_2S$  to simulate steady state conditions. Sodium sulfide was also added because it has been established at Atomic International and other laboratories that  $Na_2S$  is a catalyst in accelerating the gasification of char in molten  $Na_2CO_3$ . The gasification was carried out with 33% theoretical air. The results in Table 1 are an average of the two tests. A gas with an HHV of 156 Btu/scf was obtained. The  $CO_2$  content of this gas was considerably lower than that from the oxygen-containing wastes and is more similar to that obtained when coal or oil is gasified. In spite of the large amounts of  $Na_2S$  in the melt, no  $H_2S$  or other sulfur-containing gases ( $<30$  ppm) were detected in the off gas.

#### Nitropropane

Organic  $NO_2$ -containing compounds may well be present in small amounts in wastes which are being gasified for producing fuel. This type of compound

can emit a great deal of  $\text{NO}_x$ . In these tests, nitropropane was used to determine if it would be possible to minimize the  $\text{NO}_x$  emissions during gasification. A series of tests was run under varying conditions and with different additives. It was determined that under certain process conditions and with a specific additive, it was possible to combust nitropropane and produce a product gas containing only 6 ppm  $\text{NO}_x$ . It thus appears that the presence of organic  $\text{NO}_2$ -containing wastes will not contribute much  $\text{NO}_x$  under gasifying conditions. The composition of a typical off gas from the tests is shown in Table 1.

### Sucrose

The gasification of sucrose in pure  $\text{Na}_2\text{CO}_3$  was studied at four different stoichiometries. The melt temperature was about  $950^\circ\text{C}$ . The air feed rate (2.5 scfm) corresponded to an air superficial velocity in the gasifier of 1 ft/sec. As expected, the heating value of the gas increased as the percent theoretical air decreased. However, when the air/fuel ratio was too low, insufficient heat was released to the melt and auxiliary heating was required. This was the case with the test in which 18% theoretical air was used. The furnace was turned on during the test to maintain the melt temperature. However, at 35 and 52% theoretical air, sufficient heat was released to the melt so that the furnace could be turned off. At 72% air, excess heat was generated and had to be removed by the cooler. The relatively short experimental runs (~1 hour) did not permit a definite conclusion as to what minimum percent of theoretical air could be used in this system and still maintain melt temperature without auxiliary (furnace) heat. It appears, however, that the salt could be maintained in a molten state at least at 35% of theoretical air at which level a combustible gas with an HHV of 154 Btu/scf was being generated.

A test in which the air superficial velocity was reduced to 1/2 ft/sec yielded an off-gas virtually unchanged in composition to that when the velocity was 1 ft/sec. This suggests that residence time in the melt is not an important factor.

### Discussion

It is of interest to compare the heating value of a gas produced from a material containing a great deal of combined oxygen with that produced from a conventional fuel such as coal and fuel oil. A comparison of the heating values of gases produced by the oxygenated compounds which contain 40-50 wt % oxygen, by Kentucky No. 9 coal (7 wt % oxygen), and by No. 6 fuel oil (essentially no oxygen) using the same molten salt technology is shown in Table 3. It can be seen that the difference in heating value of the gas is relatively small in spite of the large difference in Btu content of the combustible material (12,000 Btu/lb for the coal and 19,000 Btu/lb for the fuel oil vs 7,000-9,000 Btu/lb for the oxygenated material). The small difference in heat content of the gases probably is due in part to the fact that a great deal of the oxygen is supplied by the fuel and this combined oxygen is not diluted with atmospheric nitrogen. To illustrate, the nitrogen contents of the off gas were 59% in the case of fuel oil at 20% theoretical air and only 34% in the case of sucrose at 18% theoretical air.

It has been shown that, as expected, the Btu content of the off-gas increases as the percent of theoretical air decreases. However, as was also shown (in test No. 6), there is a practical upper limit on the gas heat content which can be obtained. Above this upper limit, there will not be enough heat released to the melt to sustain the operating temperature. This upper limit can be increased somewhat by using preheated process air and by decreasing the heat losses in the gasifier with improved insulation.

The maximum waste throughput is also governed by the maximum superficial velocity of the gas through the melt. In general, the maximum superficial velocity of the inlet air has been set at 2 ft/sec. (This corresponds to a somewhat higher velocity of the product gas, depending on the fraction of total oxygen which is combined oxygen and on the composition of the off-gas.) Beyond this velocity of 2 ft/sec, entrainment of the melt becomes excessive. However, by operating at elevated pressures, the waste throughput can be significantly increased since at a given air superficial velocity, the waste throughput will be proportional to the pressure.

No sulfur-containing pollutants were observed in the off-gas when rubber was gasified. While chlorine-containing material was not gasified, in all tests in which that type of material was treated in  $\text{Na}_2\text{CO}_3$  melts with excess air, there was no trace of  $\text{HCl}$  even when the  $\text{Na}_2\text{CO}_3$  content was as low as 5 wt %. It is expected that the same results would be obtained if deficient air were used.

The results described in this paper show that the gasification of wastes in molten salts to produce a low Btu gas is technically feasible. However, an engineering evaluation leading to the economics of molten salt gasification of the various wastes has not been done and would be necessary before it can be established if this process is a practical one.

TABLE 1

## Gasification of Wastes

Test #	Waste	Temp. (°C)	Air Feed Rate (scfm)	Fuel Feed Rate (lb/hr)	% Theor (a) Air	Composition of Off-Gas (vol %)					Higher Heating (b) Value (Btu/scf)
						CO <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub>	
1	Film	1015	4.50	5.34	51	16.5	12.0	11.7	2.6	0.2	107
2	Film	958	2.50	6.58	22	16.0	18.3	14.1	5.2	1.2	179
3	Wood	951	1.00	2.08	30	14.5	20.3	21.1	3.0	0.9	181
4	Rubber	920	1.63	1.81	33	4.0	18.4	16.0	2.4	1.1	156
5	Nitropropane	1000	2.50	2.58	75	11	8	9	NM <sup>(c)</sup>	NM <sup>(c)</sup>	>55

(a) Percent of air required to oxidize material completely to CO<sub>2</sub> and H<sub>2</sub>O

(b) Calculated from composition of off-gas

(c) Not measured

TABLE 2  
Gasification of Sucrose in 100%  $\text{Na}_2\text{CO}_3$  (a)

Test #	Solid Feed Rate (lb/hr)	% Theor. Air (b)	Composition of Off-Gas (vol %)					Higher Heating (c) Value Btu/scf
			$\text{N}_2$	$\text{CO}_2$	CO	$\text{H}_2$	$\text{CH}_4$	
6	12.2	18.4	34.3	13.5	26.9	18.9	4.3	216
7	6.5	34.8	46.2	15.0	18.3	17.0	2.5	154
8	4.3	52.2	57.0	19.1	12.3	9.7	1.4	91
9	3.1	72.1	69.8	20.0	5.5	3.1	0.7	37
							$\text{C}_2$	
							1.9	
							0.8	
							0.3	
							0.1	

- (a) The melt temperature was 950-960°C. The air feed rate was 2.5 scfm  
 (b) Percent of air required to oxidize material completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$   
 (c) Calculated from composition of off-gas

TABLE 3

A Comparison of the Heating Value of Gas  
Produced from Sucrose and from Coal

OXYGENATED MATERIAL			CONVENTIONAL FUELS		
Material	% Theor. Air	HHV Btu/scf	Fuel	% Theor. Air	HHV Btu/scf
Sucrose	18	216	Fuel Oil <sup>a</sup>	20	191
Film	22	179	Fuel Oil	27	155
Wood	30	181	Coal <sup>b</sup>	35	151
Sucrose	35	154	Coal	40	138
Film	51	107	Coal	50	118
Sucrose	53	91	Coal	70	36
Sucrose	72	37			

(a) The fuel oil was a No. 6 oil. It was API gravity 18, carbon residue, 5%; ash, 0.007%; sulfur, 0.3%, hydrogen 13%.

(b) The coal was Kentucky No. 9 seam coal. The proximate analysis on a dry basis was in weight %; ash, 16.4; volatile matter, 37.6; fixed carbon, 46.0; and sulfur, 4.5. The ultimate analysis on a dry basis was: carbon, 66.3; hydrogen, 4.6; nitrogen, 1.4; sulfur, 4.5; ash, 16.4; and oxygen (by difference), 6.9.



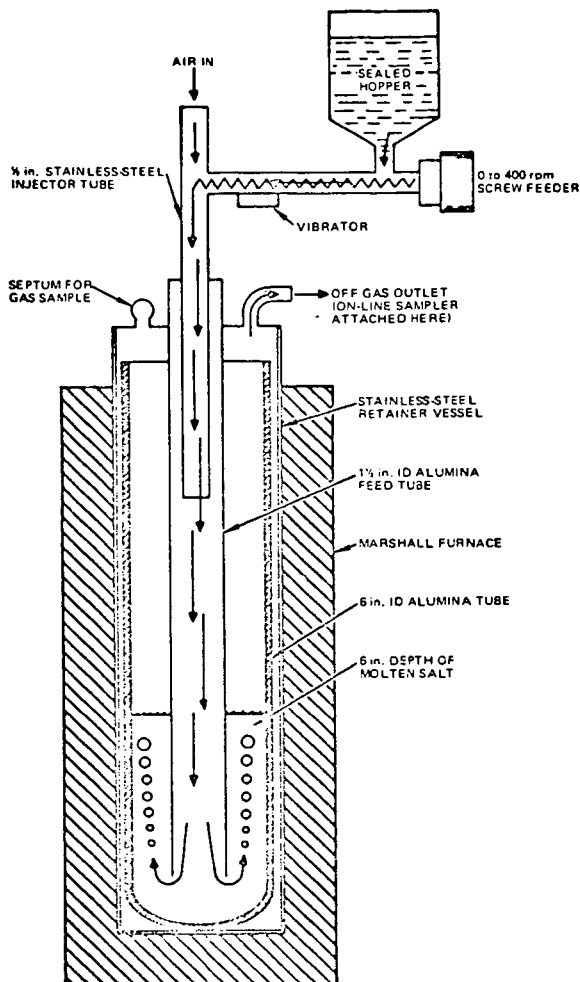


Figure 1. Bench Scale Molten Salt Gasifier Schematic

FUELS FROM WASTES - AN OVERVIEW. Bernard D. Blaustein, Pittsburgh Energy Research Center, U. S. Energy Research and Development Administration, 4800 Forbes Avenue, Pittsburgh, Pa. 15213.

Organic wastes generated in this country are estimated to exceed 800 million tons (on a dry basis) each year. This large and continually renewable energy source is beginning to be used to a significant extent. Solid, liquid and gaseous fuels with different characteristics and markets are being produced. Numerous processes for the recovery of fuels and energy from waste materials are in various stages of research, development, demonstration and commercialization. This paper will discuss these processes and fuels in order to provide an overview of this field of energy technology.